5 Passivation of zinc anodes in alkaline electrolyte: Part II. Influence of operation parameters

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Passivation of Zinc Anodes in Alkaline Electrolyte: Part II. Influence of Operation Parameters

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On the basis of a previously developed measurement method [M. Bockelmann, M. Becker, L. Reining, U. Kunz, and T. Turek, *J. Electrochem. Soc.*, 165 (13), A3048 (2018)] the influence of current load interruptions, KOH electrolyte composition, temperature, and forced electrolyte convection on the anodic passivation of zinc was investigated in this study. Our aim was to find appropriate experimental conditions which could allow a long-term usability of the zinc anode without formation of passive films. We found out that interruptions lasting several minutes during galvanostatic dissolution of zinc, as well as increasing temperature and raising concentration of OH^- ions in the electrolyte, effectively prolonged the service life of the electrode, but could not fully prevent it from passivation. On the contrary, increasing concentration of zinc oxide in the electrolyte enhanced the direct oxidation of zinc. However, application of sufficiently strong electrolyte convection and electrode overpotentials below a limiting value of about 0.1 V, allowed for electrode dissolution times of more than 1000 minutes without any indication of passive film formation. Therefore, the passivation of zinc anodes can be effectively avoided in cells with forced electrolyte convection and limited current densities.
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Due to a number of advantageous characteristics of zinc-based electrochemical systems, zinc-air batteries are considered as promising candidates for large-scale stationary energy storage devices.[1] However, electrically rechargeable alkaline zinc-based systems still suffer from low cyclability. In addition to dendrite formation and shape change during charging, one of the main causes of the short service life of these systems is the passivation of the zinc electrode during the discharging process. Several important works have been published on zinc passivation in alkaline electrolytes.[2–4] Some recent literature deals with strategies for preventing the formation of passive films on zinc anodes.[5–14] It was shown that suitable electrolyte additives or electrode coatings enabled improved cycling stabilities of zinc-based batteries.[6–13] Further groups focused on the fabrication of porous zinc electrodes in order to lower the local current densities and thus hamper the passive film formation.[14,15] Application of forced convection has also proved to be advantageous for the prolongation of the active dissolution of zinc electrodes.[16,17] However, the practicability of these strategies for electrically rechargeable zinc-based systems has not yet been sufficiently demonstrated.

Independently of the specific reaction path with corresponding reaction products, zinc oxidizes in two electron transfer steps from Zn to Zn^I and finally to Zn^{II}. The second electron transfer step is generally assumed to be the rate determining step (rds).[18,19]

$$Zn \leftrightarrows Zn^I + e^- \quad [1]$$

$$Zn^I \leftrightarrows Zn^{II} + e^- \quad \text{rds} \quad [2]$$

The kinetics of these two electron transfer steps can be expressed by the kinetic resistances R_{RC1} and R_{RC2}. During anodic zinc dissolution the kinetic resistances of Reactions 1 and 2 change and provide insight into passivation processes on the electrode. In our previous contribution[20] we presented a new testing cell which allowed simultaneous microscopic and electrochemical impedance spectroscopy (EIS) investigations of the passivation process on zinc anodes in quiescent alkaline electrolytes. An exemplary result of the EIS measurement is shown in Fig. 1a. As already discussed in our previous work,[20] the spectrum consists of two semicircles, referring to two electron transfer Reactions 1 and 2. The impedance spectroscopic data were described with an equivalent electrical circuit model consisting of two RC networks (Fig. 1a), so that the values of kinetic resistances R_{RC1} and R_{RC2} could be calculated. With the help of this method it was possible to monitor the development of the kinetic resistances R_{RC1} and R_{RC2} during the electrode dissolution and to observe changes of its surface (Fig. 1b). As a result, we were able to specify two different passivation criterions which correspond to the formation of two different passive films. Due to simultaneous microscopic observations, we found out that by applying of current densities below 110 mA cm^{-2}, the type 1 passive film begins to form at the same time when the kinetic resistance R_{RC1}, which decreased at the beginning of the measurement, passes through a minimum value and grows again. Therefore the minimum value of the kinetic resistance R_{RC1} was chosen as passivation criterion 1 (Fig. 1b). A very surprising finding was that independently of the current density in a range below 110 mA cm^{-2}, the passivation criterion 1 is always reached as soon as an electrical charge density of approx. 157 C cm^{-2} is transferred due to the dissolution of the electrode. This value corresponds to an amount of zincate ions of $8.2 \cdot 10^{-4}$ mol related to 1 cm^2 of active surface area. After reaching this amount, the type 1 passive film begins to form due to the polymerization of zincates near the electrode surface. During further dissolution of zinc, as soon as the kinetic resistance R_{RC2}, which is higher than R_{RC1} at the beginning of the electrode dissolution, falls below R_{RC1}, the formation of zinc oxide enhances. Though, the point at which the kinetic resistances of both electron transfer steps reach equivalent values, was chosen as criterion 2 (Fig. 1b). It identifies the strengthened formation of the type 2 passive film beneath the type 1 layer, which mainly consists of zinc oxide and fully prevents the electrode from further dissolution. If sufficient driving potential is available after passing the passivation criterion 2, the potential of the zinc electrode rises to that required for the oxygen evolution Reaction 3.

$$4OH^- \leftrightarrows O_2 + 2H_2O + 4e^- \quad [3]$$

The second important finding in our previous work[20] was the relation between the electrode potential and the mechanism of the passivation process. As long as the electrode overpotential did not exceed a limiting value of about 0.15 V (at anodic current densities below 110 mA cm^{-2}), the electrode passivated according to the "dissolution-precipitation" mechanism due to the accumulation of a critical value of zincate ions in the vicinity of the electrode. However, as soon as the applied current density resulted in higher overpotential than 0.15 V (at approx. 110 mA cm^{-2}), the kinetic resistance R_{RC2} was already at the beginning of the measurement higher than R_{RC1} and the electrode passivated according to the "solid-state" reactions mechanism by direct oxidation of zinc. Consequently, at higher overpotentials than 0.15 V

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Journal of The Electrochemical Society, **166** (6) A1132-A1139 (2019)

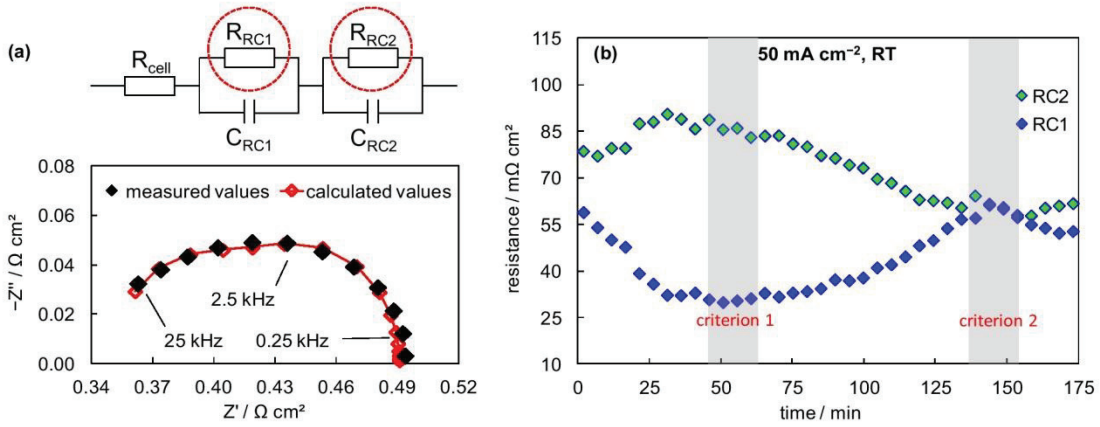

Figure 1. EIS investigations of the zinc electrode kinetics during anodic polarization at constant current density of 50 mA cm^{-2} (room temperature (RT), 30 wt% KOH with 2 wt% ZnO): (a) example of measured and calculated EIS spectra from 30 000 Hz to 20 Hz according to the equivalent electrical circuit model above. R_{cell} in the equivalent electrical circuit model represents the ohmic cell resistance, R_{RC1} the kinetic resistance of the reaction from Zn to Zn^{I} (I), R_{RC2} the kinetic resistance of the reaction Zn^{I} to Zn^{II} (II), C_{RC1} and C_{RC2} the related double layer capacities; (b) trends of R_{RC1} and R_{RC2} as a function of dissolution time. Criterion 1 area corresponds to the minimum value of the resistance R_{RC1} and identifies the beginning of the type 1 film formation. The time at which both ohmic resistances R_{RC1} and R_{RC2} reach equivalent values was chosen as criterion 2. (Cf. Bockelmann et al.[20] Fig. 5).

the passivation criterion 2 was reached directly at the beginning of the electrode polarization.

In the majority of publications on zinc passivation at constant current, the passivation was determined by the onset of oxygen evolution and the corresponding potential jump. Contrary to that definition, which indicates the completed passivation process, the passivation criterions 1 and 2 developed in our previous work allow the identification of the starting point of the film formation and not only of the ending point. Thus our earlier findings contributed to a better understanding of the overall mechanism of passivation reactions on a zinc anode in alkaline electrolyte, but it did not provide suggestions how to avoid the formation of the passive films and to prolong the active state of the electrode. However, this knowledge would be essential for the development of a long-life zinc-based electrical storage system. Therefore, it is highly important to investigate the influence of different operation parameters of a zinc-based battery like temperature, electrolyte concentration or forced electrolyte convection on the dissolution process of the zinc anode in order to find optimal conditions which could prevent zinc from passivation.

Only little information about the relationship between temperature and passivation time is available in the literature.[2] The main message of published scientific work on this topic is that increasing temperature slows down the passivation process and prolongs the service life of zinc anodes.[21–23]

The effect of electrolyte composition on the passivation process on zinc anodes was studied by several groups.[21,23–26] The majority of them investigated the variation of the so-called limiting current density i_{lim} which induced the onset of oxygen evolution reaction within a defined period of time in electrolytes with different concentrations of KOH and ZnO. They reported that i_{lim} reached a maximum at a KOH concentration of 7 mol L^{-1}, which corresponds to approx. 30 wt%. This result led to the conclusion that the specific conductivity of KOH solutions, which is highest at 7 mol L^{-1}, had a significant effect on the limiting current density. Measurements with additional ZnO in the electrolyte corroborated that assumption. A higher amount of ZnO reduced the value of i_{lim}, which was believed to be caused by the negative effect of ZnO on the specific conductivity of the electrolyte.

Some research groups[22,23,27–29] also investigated possibilities to reactivate passivated zinc anodes, but their results are generally contradictory. One interesting observation was made by Landsberg and Bartelt[30] who described that short interruptions with no current flowing during galvanostatic dissolution of zinc caused a nearly complete reactivation of the electrode.

Furthermore, only limited information exists about the influence of electrolyte convection on the passivation of zinc electrodes. Powers postulated that the formation of type 1 passive film could be prevented in the presence of forced convection.[31] However, the appearance of type 2 passive film was not affected by the electrolyte flow. Further work on this topic did not provide any unambiguous results on the effect of convection on zinc passivation.[2]

Therefore, the main aim of the present contribution is to prove the hypotheses of other groups using our newly developed investigation method and to reach greater clarity on the matter of zinc passivation. We furthermore intend to find the optimal operation conditions for a zinc anode in alkaline electrolyte by varying the temperature, the electrolyte composition, and the electrolyte volume flow rate in order to prevent zinc from passivation.

Experimental

A detailed description of the used testing cell, materials and methods was provided in our previous contribution.[20] The employed zinc specimens (Grillo-Werke AG, Germany) had a thickness of 3 mm and an active surface area of 28 mm^2. As counter electrode (CE) an in-house produced silver-based oxygen depolarized cathode was used,[32] while the reference electrode (RE) was a reversible hydrogen RE (mini-Hydroflex, Gaskatel, Germany). The testing cell had total dimensions of 90 mm × 40 mm × 15 mm while the gap between the zinc specimen and the CE was 7 mm. During measurements in quiescent electrolyte, the electrolyte volume in the cell amounted to 10 mL.

As for the previous measurements, galvanostatic EIS spectra were recorded every 180 s during anodic dissolution of zinc at constant current with the same DC current. However, no microscopic images were taken during the present work, because the passivation process could now be observed and interpreted on the basis of EIS spectra only. Therefore, no glass window was integrated into the CE. All measurements were performed in 30 wt% KOH electrolyte with 2 wt% ZnO, apart from those used to examine the effect of variable electrolyte composition. For the variation of temperature between 17°C and 40°C during measurements in quiescent electrolyte, the measurement setup was placed into a temperature chamber. Furthermore, iR compensation of measured potentials of the zinc electrode was carried out on the basis of initially determined ohmic resistances from EIS data.

For passivation investigations in the presence of forced convection, the testing cell was extended with tubes for the electrolyte circulation.

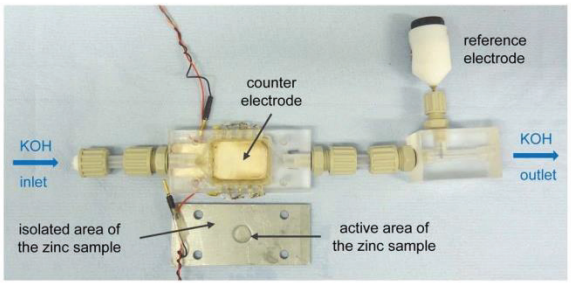

Figure 2. Measurement setup for investigations of zinc passivation in flowing electrolyte. The testing cell had total dimensions of 90 mm × 40 mm × 15 mm, extended with tubes and electrolyte tank. The electrolyte volume was 500 mL, the zinc sample had a thickness of 3 mm and an active area of 28 mm^2.

For that reason the reference electrode was positioned at the outlet manifold of the cell (Fig. 2). The electrolyte flow rate was varied between 65 mL min^{-1} and 195 mL min^{-1} with the help of a laboratory diaphragm liquid pump (KNF, NF 1.25, Germany). The storage tank for the electrolyte had a volume of 500 mL.

Results and Discussion

Influence of interruptions of the current load.—In order to prove the finding of Landsberg and Bartelt,[30] that short interruptions with no current flowing during galvanostatic dissolution of zinc led to much longer passivation times, we investigated the influence of the duration of interruptions on the transferred electrical charge for an anodic current density of 70 mA cm^{-2} in 30 wt% KOH electrolyte with 2 wt% ZnO at room temperature. The interruptions of the current load were performed after every combination of anodic dissolution of zinc for 180 s and the EIS measurement. Our results in Fig. 3 show that the interruptions indeed increase the charge values corresponding to both passivation criterions (determined by multiplying the dissolution time until the passivation criterions are reached with the applied current density), but only up to a certain amount. The maximum electrical charge value could be increased from 150 C cm^{-2} to about 200 C cm^{-2} for passivation criterion 1 and from 325 C cm^{-2} to approx. 450 C cm^{-2} for passivation criterion 2. The most effective increase of the charge value could be achieved with interruptions of 5 minutes. Longer durations did not show any further significant improvement of the discharge behavior. Consequently, we conclude that passive films on zinc,

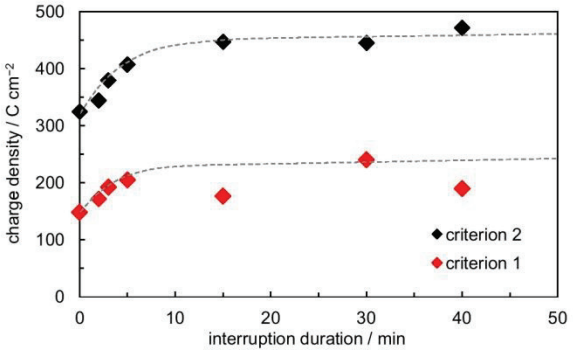

Figure 3. Influence of interruptions on the maximum value of transferred electrical charge density according to passivation criterions 1 (red) and 2 (black) during anodic passivation of zinc (current density 70 mA cm^{-2}, room temperature, 30 wt% KOH with 2 wt% ZnO). The interruptions were performed after 180 s of anodic polarization with constant current and the following recording of a galvanostatic EIS spectrum with the same DC current.

formed according to the "dissolution-precipitation" mechanism, could probably partially dissolve, as it was stated e.g. by Dirkse,[23] but that the main increase of the transferred electrical charge is more likely caused by the rise of the hydroxide ions concentration in the vicinity of the electrode during the interruptions. Otherwise, the transferred electrical charge would steadily increase with raising interruption durations, unlike the progression in Fig. 3. Thus, higher OH^- concentration presumably hampers the polymerization of zincates and delays the formation of the passive films. Although it is possible to prolong the service life of a zinc anode by application of interruptions to some extent, our measurements clearly show that passivation cannot be completely avoided.

Influence of electrolyte composition.—Fig. 4a shows the transferred electrical charge density until the passivation criterions are reached in dependence of the KOH concentration for the applied anodic current density of 70 mA cm^{-2} at 25°C. Contrary to previous work of other groups,[21,23,24,26] the transferred charge density was found to increase steadily with rising KOH concentration and did not show the expected maximum at 30 wt% KOH. These results again support our assumption that higher concentrations of OH^- ions suppress the polymerization of zincates and delay the formation of the passive films, although the specific conductivity of the electrolyte reduces at KOH concentrations exceeding 30 wt%. However, the discrepancy between our work and the studies of other groups could be also due to different experimental conditions. In our experiments the passivation of zinc proceeds within hours until the oxygen evolution reaction sets in, in the experiments of other groups within several minutes.[21,24,26] Thus, it is questionable whether it was possible to build up a passive film in this short period of time. It is very likely that the applied current density in these measurements was higher than the maximum possible diffusion limiting current density. Therefore, it is probable that the potential jump occurred due to a lack of OH^- ions in the vicinity of the electrode and not due to the completed passivation process. This could also explain why an optimum for i_{lim} in 30 wt% KOH electrolyte was observed, since the rising viscosity at higher alkali concentrations might hamper the mobility of OH^- ions and reduces the maximum possible diffusion limiting current density.

Another interesting result is shown in Fig. 4b. The maximum transferred electrical charge that corresponds to passivation criterion 1 varies only slightly at different concentrations of ZnO in 30 wt% KOH electrolyte for an anodic current density of 70 mA cm^{-2} at 25°C. This means that mainly electrochemically formed zincate ions polymerize in the vicinity of the electrode, building up the type 1 passive film. The influence of chemically dissolved ZnO, by contrast, has only little influence on the polymerization process of zincates. However, higher ZnO concentrations considerably reduce the transferred electrical charge corresponding to the passivation criterion 2, which corresponds to the enhanced formation of type 2 passive film. As it was discussed in our previous contribution, the type 2 passive film is primarily dependent on the potential of the zinc electrode. Therefore, we expected to observe higher overpotentials at the anode in electrolytes with increasing concentration of zincate ions. However, in contrast to our expectation, the potential of a non-passivated zinc electrode at the beginning of the anodic dissolution was not affected by the amount of ZnO in the electrolyte, as shown in Fig. 4c. Thus, we are not able to provide a clear explanation for the dependence of passivation criterion 2 on the concentration of zincate ions in the electrolyte. One possible reason could be the complexation of OH^- ions by addition of ZnO to the KOH solution which was shown by decreasing specific conductivity of KOH electrolyte with growing concentration of zincate ions.[33] Therefore, the reduced availability of OH^- ions could provoke the direct oxidation of the electrode and enhance the formation of the type 2 passive film. On the other hand, it remains incomprehensible why the reduced availability of OH^- ions affects the formation of type 2 passive film but has no influence on type 1 passive film. Microscopic observations of the electrode could provide important information regarding this question. However, this was not the scope of the present work. In summary, it can be said, that the electrolyte composition

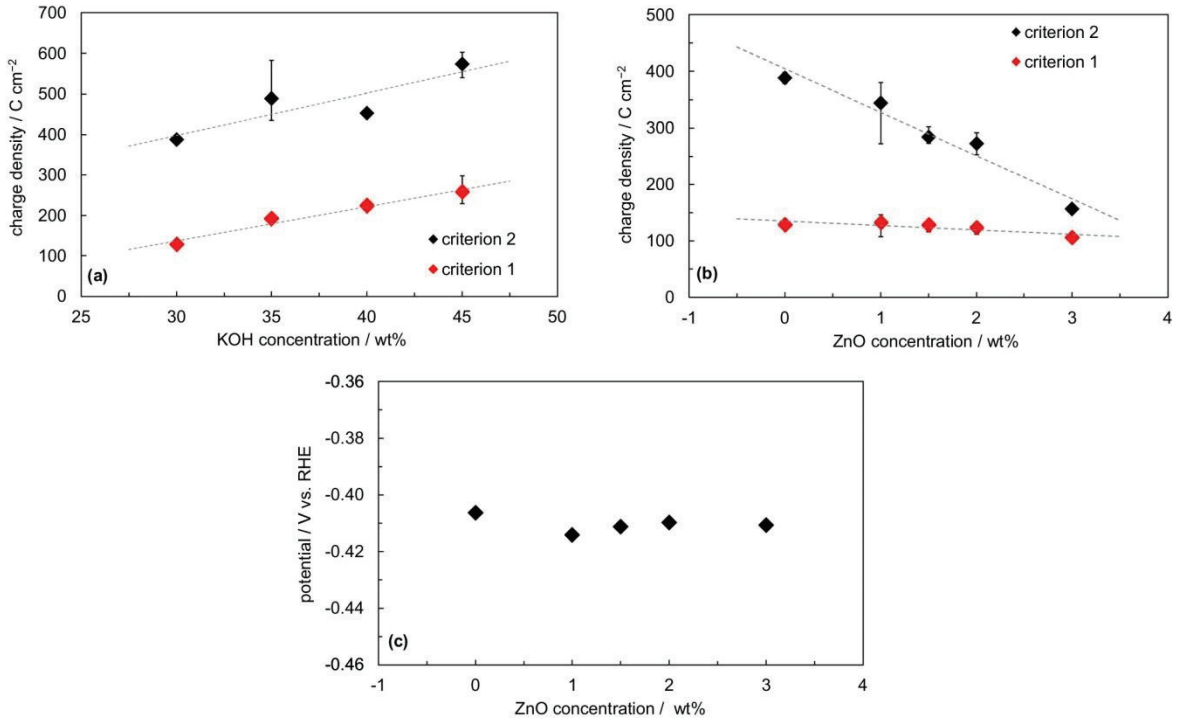

Figure 4. Influence of the electrolyte composition on the dissolution of a zinc electrode at a current density of 70 mA cm^{-2} and 25°C: (a) effect of varying KOH concentration and (b) ZnO concentration in 30 wt% KOH electrolyte on the transferred electrical charge density corresponding to passivation criterions 1 (red) and 2 (black); (c) effect of varying ZnO concentration in 30 wt% KOH electrolyte on the operating potential of a non-passivated zinc electrode at the beginning of the galvanostatic dissolution vs. RHE.

has a significant influence on the service life of a zinc anode. Higher OH^- concentrations prolong the active state of the electrode during its dissolution, whereas the addition of ZnO to the electrolyte quite significantly enhances the formation of the type 2 passive film.

Influence of temperature.—One of the most important operation parameters of an electrochemical storage system is the temperature. Consequently, we also investigated the effect of temperature on the transferred electrical current density according to passivation criterions 1 and 2. It can be seen from Fig. 5a that an increasing temperature during dissolution of zinc at different current densities has no noteworthy influence on passivation criterion 1. Since adsorption phenomena from solutions are usually dependent on temperature,[34] this result suggests that type 1 passive film most likely does not arise due to the adsorption of oxidation products of zinc on the electrode surface. This supports our assumption that type 1 passive film rather forms due to polymerization of zincate ions in the supersaturated region near the electrode due to a lack of water molecules and hydroxide ions.[20] Fig. 5a shows further that in contrast to passivation criterion 1, criterion 2 is dependent on temperature and the transferred electrical charge density increases with rising temperature. This result confirms the conception that formation of type 2 passive film proceeds according to "solid-state" reaction mechanism, which includes the adsorption of ZnO_{ad} species.[2,20]

Interestingly, the influence of temperature on passivation criterion 2 strongly reduces for higher dissolution current densities (Fig. 5a). When plotting the trend lines for the results of criterion 2 at different current densities, it is noticeable that they all intersect with the trend line for criterion 1. This raises the question as to how the passivation process proceeds at temperatures below the point of intersection. In Fig. 5b the development of kinetic resistances R_{RC1} and R_{RC2} is presented as function of time for dissolution current density of 70 mA cm^{-2} and a temperature of 21°C, which approximately corresponds to the point of intersection. With regard to these results, the passivation proceeds according to the "dissolution-precipitation" mechanism, as described in more detail in our earlier work.[20] The kinetic resistance R_{RC1} decreases at the beginning of the dissolution of zinc, reaches a minimum and rises again after about 30 min, passing the passivation criterion 1. After 65 min, R_{RC1} and R_{RC2} reach the same value, which corresponds to passivation criterion 2. During further zinc dissolution the electron transfer step (1) becomes slower than the reaction step (2) and the direct oxidation of the electrode is enhanced. All measurements presented in Fig. 5a show similar trends of the kinetic resistances R_{RC1} and R_{RC2} and the passive film forms according to the "dissolution-precipitation" mechanism. However, after lowering the temperature to 17°C (Fig. 5c), R_{RC1} is already at the beginning of the measurement higher than R_{RC2}. This means that below a certain temperature between 21°C and 17°C, the electrode overpotential reaches a critical value and the passivation rather proceeds according to the "solid-state" reaction mechanism. In order to verify this conclusion, the overpotentials of zinc electrodes at the beginning of the galvanostatic dissolution at different temperatures should be regarded (Fig. 5d). Filled diamonds in Fig. 5d illustrate passivation measurements according to the "dissolution-precipitation" mechanism, hollow diamonds those according to the "solid-state" reactions mechanism. As expected, the overpotentials of the electrode at an applied current density of 70 mA cm^{-2} shift to higher values with decreasing temperature. As soon as an overpotential value of approx. 0.1 V is exceeded, the formation of the passive film according to the "solid-state" reactions mechanism can be observed (hollow diamonds in Fig. 5d). Additionally, Fig. 5d shows, that the current density of 110mA cm^{-2} results in reaching the critical overpotential also at higher temperatures. However, increasing temperature has obviously a positive effect on the kinetics of the first electron transfer step (1) and promotes the

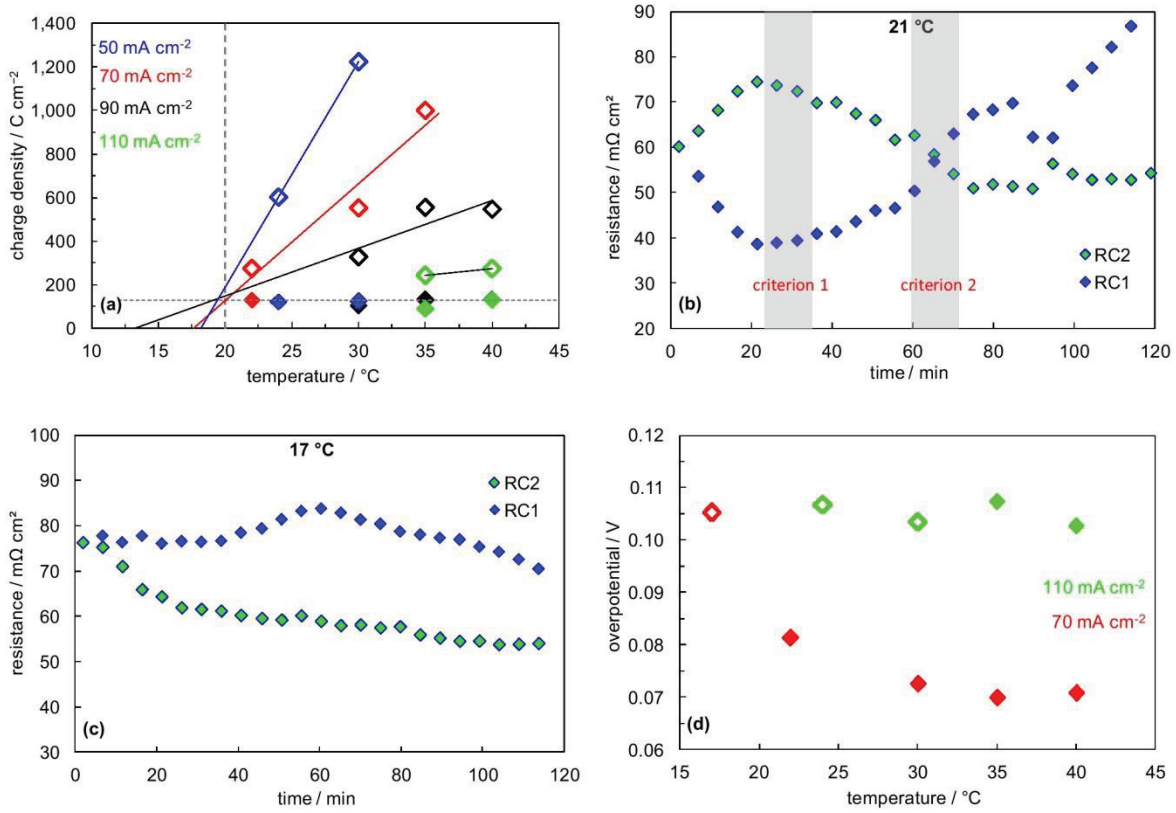

Figure 5. Influence of temperature on the passivation of zinc in 30 wt% KOH electrolyte with 2 wt% ZnO at different applied anodic current densities: (a) influence of temperature on the transferred electrical charge according to passivation criterion 1 (filled diamonds) and criterion 2 (hollow diamonds) at current densities between 50 mA cm^{-2} and 110 mA cm^{-2}; (b) trends of R_{RC1} and R_{RC2} as a function of dissolution time at 70 mA cm^{-2} and 21°C. The electrode passivates according to the "dissolution-precipitation" mechanism and passivation criterions 1 and 2 are identified; (c) trends of kinetic resistances R_{RC1} and R_{RC2} at 70 mA cm^{-2} and 17°C. Already at the beginning of the measurement R_{RC1} is higher than R_{RC2} and the electrode passivates according to the "solid-state" reaction mechanism due to direct oxidation of zinc; (d) overpotentials of the zinc electrode at the beginning of the dissolution with 70 mA cm^{-2} and 110 mA cm^{-2} at different temperatures. Filled diamonds describe passivation conditions at which the film formation proceeds according to the "dissolution-precipitation" mechanism. Hollow diamonds illustrate conditions at which the electrode passivates according to the "solid-state" reactions mechanism.

passivation process of zinc electrodes corresponding to the "dissolution-precipitation" mechanism, which can be seen due to filled diamonds at temperatures from 35°C. In previous work, the "solid-state" reaction mechanism was found to proceed enforced after exceeding a limiting overpotential of 0.15 V.[20] The deviation between these and the present results is mainly caused by the iR compensation of the measured potentials in this work. Finally, it can be said that higher temperatures prolong the usage of the zinc electrode by reducing the electrode overpotential and suppressing the formation of the type 2 passive film. Nonetheless, it is not possible to completely avoid the passivation of zinc because the formation of type 1 film is not dependent on temperature and occurs after the critical amount of zincate ions is released during the electrode dissolution.

Influence of forced convection.—It was shown that application of interruptions, variation of electrolyte composition and temperature lead to an extension of the useful life of the zinc electrode, but a complete avoidance of the passivation process could not yet be achieved. Following the work of Powers[31] we investigated the passivation of zinc in flowing electrolyte in an attempt to suppress the appearance of the type 1 passive film. Moreover, reduction of the overpotential below the maximum permissible value could probably also prevent the formation of the type 2 passive film. Consequently, a current density of 70 mA cm^{-2}, a temperature of 22°C, an electrolyte with 30 wt% KOH and 2 wt% ZnO and an electrolyte flow rate of 65 mL min^{-1} were chosen as starting values for the reaction conditions.

Fig. 6a shows trends of the kinetic resistances R_{RC1} and R_{RC2} as a function of the dissolution time. It can be seen that the kinetic resistance R_{RC1} decreases at the beginning of the experiment until a minimum value is reached. Then R_{RC1} grows again while R_{RC2} decreases (passivation criterion 1). After a duration of 100 min, the kinetic resistance R_{RC1} reaches higher values than R_{RC2} (passivation criterion 2). After 260 min the potential of the electrode finally raises to positive values caused by the oxygen evolution Reaction 3. Obviously, it was not possible to suppress the passivation of zinc even in presence of convection at 65 mL min^{-1}, since both passivation criterions and the final potential jump could be observed at these conditions.

However, Fig. 6b shows that at a higher electrolyte flow rate of 140 mL min^{-1} the passivation criterion 1 is still observed, but the trends of R_{RC1} and R_{RC2} do not intersect and R_{RC1} remains always lower than R_{RC2} over 1000 min of dissolution. Therefore the passivation criterion 2 is not apparent for higher electrolyte flows. After 1000 min the experiment was finished without any indication of passivation. Moreover, the electrode potential shifts even to more negative values during the investigation probably due to the enlargement of the specific surface area of the electrode (Fig. 6c). Consequently, a zinc electrode is able to preserve its activity during a long-term dissolution measurement as long as the electrolyte flow rate is high enough. However, it remains

Journal of The Electrochemical Society, **166** (6) A1132-A1139 (2019)

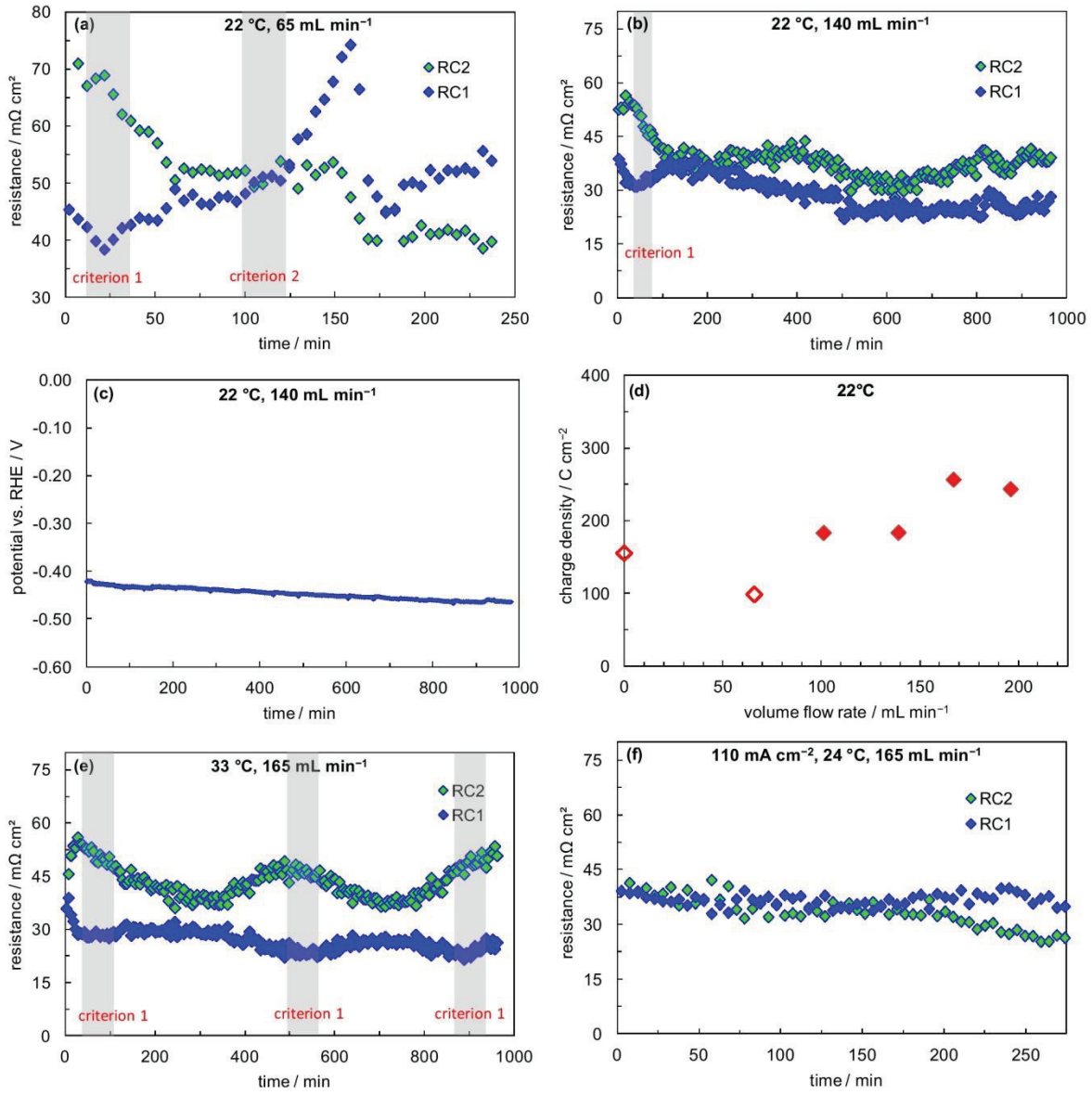

Figure 6. Influence of forced convection on the passivation of zinc in 30 wt% KOH electrolyte with 2 wt% ZnO: (a) trends of R_{RC1} and R_{RC2} as a function of dissolution time at a current density of 70 mA cm^{-2}, a temperature of 22°C and an electrolyte volume flow rate of 65 mL min^{-1}. Passivation criterion 1 and criterion 2 are observed despite the presence of convection; (b) trends of R_{RC1} and R_{RC2} as a function of dissolution time at 70 mA cm^{-2}, 22°C and a flow rate of 140 mL min^{-1}. Only passivation criterion 1 is observed at these conditions; (c) potential curve of a zinc electrode vs. RHE during galvanostatic dissolution with 70 mA cm^{-2} at 22°C and a flow rate of 140 mL min^{-1}; (d) dependence of the transferred electrical charge density according to passivation criterion 1 on the electrolyte volume flow rate at 22°C. Hollow diamonds describe conditions which lead to zinc passivation, filled diamonds illustrate passivation free measurements; (e) trends of R_{RC1} and R_{RC2} as a function of dissolution time at 70 mA cm^{-2}, 33°C and a flow rate of 165 mL min^{-1}. Minima of R_{RC1} are observed three times during 1000 min dissolution which indicates the formation of three different type 1 passive films; (f) trends of R_{RC1} and R_{RC2} as a function of dissolution time at 110 mA cm^{-2}, 24°C and a flow rate of 165 mL min^{-1}. R_{RC2} reaches lower values than R_{RC1} despite the presence of high convection and the electrode passivates due to direct oxidation of zinc, caused by exceeding the maximum permissible overpotential.

to be explained what the appearance of the first passivation criterion at 140 mL min^{-1} causes (Fig. 6b). For this reason, the effect of the electrolyte flow rate on the passivation process was systematically studied. Fig. 6d shows the influence of the volume flow rate between 65 mL min^{-1} and 195 mL min^{-1} on passivation criterion 1. Hollow diamonds illustrate measurements in which a passivation of the electrode was detected; filled diamonds describe experiments without any indication of electrode passivation even after long-term dissolution. It is evident that the maximum transferable electrical charge until criterion 1 is reached, has about the same value as during measurements without convection and increases only slightly with higher flow rates. In contrast to the findings of Powers,[31] who described the complete

avoidance of type 1 passive film in flowing electrolyte, we attribute the increase of R_{RC1} after passing through the minimum in Fig. 6b to the appearance of a type 1 passive layer, which is assumed to form in the diffusion boundary layer of the flowing electrolyte. On the other hand, the electrode stays active even after 1000 min and R_{RC1} remains lower than R_{RC2}, which means that the formed type 1 passive film does not provoke the occurrence of any type 2 passive layer. This can be attributed to the continuous removal of type 1 passive film through the electrolyte flow. Consequently, we explain the anodic zinc passivation process in alkaline electrolyte in the presence of forced convection as follows. First, zincate ions accumulate at the vicinity of the electrode and form loose and veil-like type 1 passive film by polymerization. During further dissolution of the electrode, the distance between the zinc surface and the type 1 passive film grows due to the electrode removal until the passive film can be carried away by the electrolyte flow. Raising electrolyte velocity increases the shear stress on the electrode and favors the interference with the type 1 passive film. It is therefore obvious that a minimum electrolyte flow rate is required in order to inhibit the passivation process.

However, if the assumption described above is correct, the type 1 passive film would arise anew every time it is carried away by the electrolyte flow and criterion 1 should be observable several times during the long-term investigation of zinc dissolution. Indeed, a passivation experiment conducted at 33°C and 165 mL min^{-1} (Fig. 6e) shows particularly clearly the presence of three minima of the kinetic resistance R_{RC1} with the subsequent increases, which correspond to the formation of three different type 1 passive films. Consequently, sufficiently strong forced convection would remove the periodically formed loose and veil-like type 1 passive film and prevent the appearance of the dense and coherent type 2 passive film underneath the first passive layer. In order to verify this conclusion and to find the cause for the appearance of the minima of R_{RC1} during the dissolution of the electrode in flowing electrolyte, additional optical measurements are required, which, however, were not within the scope of this work.

Notwithstanding the encouraging result described above, it is highly important to comply with the limiting zinc electrode overpotential, or maximum permissible current density, in order to avoid the direct oxidation of zinc. The trends of the kinetic resistances R_{RC1} and R_{RC2} in Fig. 6f show that a current density of 110 mA cm^{-2} at 24°C leads to enhanced direct oxidation of zinc despite a high electrolyte flow rate of 165 mL min^{-1}, similar to experiments in quiescent solution (Fig. 5d). Already at the beginning of the measurement R_{RC2} is of the same value as R_{RC1} and continues to decrease during further dissolution. After about 270 min the EIS signal quality became increasingly poorer, thus determination of kinetic resistances was no longer possible. The measurement was finally aborted after 340 min due to the onset of the oxygen evolution reaction. Obviously, only the combination of electrolyte convection and a limitation of the electrode overpotential allow a complete avoidance of passivation.

Conclusions

On the basis of a previously developed method,[20] the influence of current load interruptions, KOH electrolyte composition, temperature, and forced electrolyte convection on the anodic passivation of zinc was investigated by means of electrochemical impedance spectroscopy during galvanostatic dissolution of the zinc electrode. It was found that short current interruptions of 5 minutes during the measurement lead to approx. 35% higher transferable electrical charge before the formation of passive films starts. A total avoidance of passivation could not be reached by application of current interruptions. An increase of temperature had no influence on the appearance of type 1 passive film whereas the rate of formation of type 2 film was significantly reduced. This means that increasing temperature in fact slows down the passivation process. However, contrary to the main message of previously published scientific work on zinc passivation, the onset of passivation cannot be delayed or even avoided by increasing the temperature, and the service life of a zinc electrode, especially in a rechargeable zinc-based battery, can therefore not be prolonged at higher operation temperatures. Investigations of the influence of the electrolyte composition on zinc passivation provided results which do not agree with the studies of other groups. It was previously reported that the specific conductivity of the electrolyte would have a positive effect on the retardation of the passivation process, and the 30 wt% KOH solution would have proven to be the optimum electrolyte. The results of the present work showed, however, that raising the KOH concentration from 20 wt% to 45 wt% resulted in doubling of the useful life of the electrode before passivation started, which is attributed to the higher availability of OH^- ions preventing zincate polymerization. Consequently, it would be beneficial to use higher concentrated KOH electrolytes for anodic dissolution of zinc electrodes, but the specific conductivity of the electrolyte seemed to have very little if any impact on the passivation process. Addition of ZnO to the electrolyte enhanced the formation of the type 2 passive film, probably due to a lower availability of OH^- ions. Since it is a general aim to increase the concentration of ZnO in the electrolyte (15.7 wt% ZnO in 30 wt% KOH solution are possible[35]) in order to improve the energy density of a zinc-based alkaline energy storage systems, the influence of this high amount of ZnO on the passivation process should be examined.

While only a partial improvement of the passivation behavior can be achieved by adjustment of temperature and electrolyte composition, forced electrolyte convection plays a decisive role in suppressing the passivation of a zinc anode. We could show that at sufficiently high electrolyte flow rates and moderate anodic current densities, the electrode can be operated over 1000 min without any indication of passivation. One possible explanation for this result is that at high electrolyte flows forming type 1 passive film can be removed early enough so that the appearance of a type 2 passive film underneath the first layer can also be avoided. In order to prove this assumption, additional optical in situ investigations of the electrode are required. However, our results show additionally that the avoidance of zinc passivation at high electrolyte flow rates is only true if a maximum permissible electrode overpotential, which was found to be approx. 0.1 V, is not exceeded. Otherwise, a direct oxidation of zinc would proceed despite strong electrolyte convection. This is a very important knowledge for the operation of zinc-based alkaline batteries which could be gained in our work. In summary, it is possible to select optimal operation conditions during the discharge of zinc-based alkaline batteries based on the present study which guarantee a long-term usage of zinc anodes due to the avoidance of their passivation. For future investigations it would be important to include optical observations which could provide insight into the zinc electrode passivation processes during the interruptions, or help understanding the mode of action of passivation-suppressing additives.

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